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(54) Title: SOLID PARTICLE MANUFACTURE

(57) Abstract

A method for making solid particles containing a mixture of solid crystalline metal oxide and/or salt compounds comprising the steps of: admixing particulate metal compounds to form a dry solids blend of at least two different crystalline solids; comminuting coarse, dry blended particulate solids, preferably in a micronizer mill by impelling the solids blend with high pressure dry inert gas against a hard plate surface, thereby producing finely-divided crystalline solids; recovering a comminuted solids blend having an average particle size of about 1-5 microns; forming an aqueous slurry of the comminuted solids blend, preferably having a weight ratio of free water to solids less than 2:1; drying the aqueous slurry to form agglomerated particles having an average size range greater than about 20 microns; and recovering dry agglomerated particles having enhanced attrition resistance and particle size uniformity. This manufacturing method is particularly useful in making multi-component contact solids.

SOLID PARTICLE MANUFACTURE

FIELD OF THE INVENTION

This invention relates to methods for making mixed crystalline solid particles by dry-milling a mixture of coarse particulate metal oxide and/or metal salt raw materials, forming a slurry of the finely-divided, co-milled particles and drying the slurried materials to form agglomerated larger particles.

BACKGROUND OF THE INVENTION

Various manufacturing processes for contact solids comprising various metal compounds and mixtures are known in the industry. Solids milling, particle separation, slurrying and drying techniques are well known, and can be performed in batch operations, semi-batch or continuously.

Metal oxide or metal salt raw materials are generally available as a commodity having relatively coarse, non-uniform particles, thus requiring size reduction or comminution prior to making contact solids containing such raw materials. Contact solids products for use as industrial catalysts, sorbents, etc., often require close control of particle size distribution and other physical properties, such as attrition resistance. Mechanical strength is especially important in those industrial process, such as fluidize catalytic cracking (FCC) or other unit operations wherein the contact solids are subject to mechanical handling. Attempts to improve attrition properties have often relied upon binder materials to impart the desired mechanical properties to the chemical agents. US 4,755,499 (Neal et al) relates the importance of attrition resistance in fluid bed solids.

US 5,559,067 (Lerner et al) describes in situ processes for making improved zeolitic fluid cracking catalyst by spray drying a mixture of hydrous kaolin, gibbsite and spinel, essentially free from metakaolin, calcining the resulting microspheres to convert the hydrous kaolin to metakaolin. The gibbsite crystals are ground to less than 5 microns prior to slurrying.

In US Patent 5,498,731 (Tsurta et al) oxide catalyst is prepared by: reacting a pentavalent vanadium compound and a pentavalent phosphorus compound in an organic solvent in the presence of a reducing agent capable of reducing the pentavalent vanadium to the tetravalent state to produce the crystalline composite oxide particles containing tetravalent vanadium and pentavalent phosphorus; dry-pulverizing the obtained crystalline composite oxide particles in a high-speed gas flow; mixing the pulverized particles with an aqueous solution containing tetravalent vanadium and pentavalent phosphorus to form a slurry, spray-drying the slurry and then calcining.

SUMMARY OF THE INVENTION

A novel method for making mixed crystalline solid particles has been found. In the prefered embodiments, an intimate mixture of metal oxides and/or metal salts is formed by dry milling an admixture of coarse solid components to form a finely divided blend of comminuted particles having an average size less than 5 microns (µ), typically less than about 2µ. An aqueous slurry of the admixed solids blend can be spray dried to form larger aggregates having an average size of at least 20µ having superior attrition resistance and uniform particle distribution. The products are useful as contact solids, such as sorbents or catalysts.

DETAILED DESCRIPTION OF THE INVENTION

In the following description, units are given as parts by weight and metric units unless otherwise indicated.

Various combinations of metal oxides and salts have been found to be useful for co-milling according to the present invention. For instance, zinc oxide, calcium sulfate (gypsum), silica, basic magnesium silicate (talc), titanium dioxide, USY synthetic faujasite and ZSM-5 zeolites, hydrotalcite, bentonite and various other clays. These metal oxide/salt components may be useful in hydrocarbon conversion catalysis, NOx/SOx sorption and other contact processes. For instance US 4,640,825 (Rosenberg) describes ZnO particles in a spray dryer and employed for SOx abatement.

The contact solids compositions made by this invention may include a combination of inorganic oxides or salts with an inorganic binder. Desirable inorganic oxides include a member selected from the group consisting of oxides or hydroxides of aluminum, calcium, cobalt, copper, iron, magnesium, molybdenum, silicon, titanium, vanadium, zinc, tungsten, strontium, nickel, manganese, zirconium, barium, members of the lanthanide series and mixtures thereof. The contact solid compositions may be self-bound or may include a binder component to "glue" the inorganic oxides together into the desired shape, such as spheroidal particles. Depending on the application, different binding systems are used, and binders may be added to co-milled metal oxides/salts prior to forming the aquous slurry.

For example, in more severe high temperature applications such as fluid cracking catalyst (eg- 700-820°C), a hydrothermally stable inorganic binder such as aluminum chlorohydrol or peptized alumina is used.

Effective inorganic binders include sols of aluminum such as aluminum chlorohydrol, peptized aluminas, sols of

silica, colloidal silicas, sols of titanium, sols of zirconium clays such as bentonite, calcined kaolinite, kaolinite, metakaolin, montmorillonite, chlorite, talc, and mixtures of these. Desirable inorganic binders include a sol of aluminum, peptized alumina, a sol of silica, colloidal silica, a sol of titanium, a sol of zirconium, a clay, and mixtures thereof.

Manufacturing Logistics - The method for making solid particles according to one aspect of the invention provides the intimate mixture of solid crystalline metal compounds by the steps of:a) admixing particulate metal compounds to form a dry solids blend of at least two different crystalline solids; b) dry milling the blended solids to produce finely-divided crystalline solids; c) recovering from the dry milling step a comminuted solids blend having an average particle size of about 1-5 microns; d) storing the recovered comminuted solids blend in a dry storage container for subsequent completion of manufacture; e) transporting a measured portion of the comminuted solids blend from the storage container to a manufacturing facility; f) forming an aqueous slurry of the transported, comminuted solids blend; g) drying the aqueous slurry to form agglomerated particles having an average size range greater than about 20 microns; and h) recovering dry agglomerated particles having enhanced attrition resistance and particle size uniformity.

This technique lends itself well to flexible manufacturing facilities wherein several different preblended materials comprising the co-milled crystalline materials are stored under dry conditions until required for entry into the manufacturing stream. Online blending of multiple pre-blended components by conveyors or the like can be controlled from a console associated with the

slurrying step. Surfactants are added advanteously with the slurried components at this point in the manufacturing process.

For example a mixture of zinc oxide and titanium dioxide in a fixed weight ratio of 1.5:1 $ZnO:TiO_2$ can be pre-blended and stored for later incorporation into a variety of differenct contact solids formulations.

<u>Dry Milling Techniques</u> - Existing dry milling and particle separation equipment can be employed in the comminuting step. US 3,531,310 (Goodspeed et al) provides a summary of prior art "micronizer" technology is given in Col. 4 and exemplifies this type of dry milling. A typical micronizer machine is made by Sturdevant and performs dry milling by impelling the solids blend with high pressure dry inert gas against a hard plate surface thereby producing finely-divided crystalline solids and recovering an intimate comminuted solids blend having an average particle size of about 1-5µ or smaller. Typical micronizer operations produce recovered particles predominantly less than 2µ size. It is understood by those skilled in the comminuting art that substantially equivalent results can be obtained by alternative dry milling techniques and subsequent particle separation and recovery. Typically, the comminuting step is conducted at ambient temperature or less than 25°C, depending upon the frangibility of the coarse particulates in the feed. Air or inert gas is usually employed as the source of fluid engergy for the micronizer milling. Dry gas having a dew point of less than -50°C can assure that no free water is added to the solids during milling.

<u>Slurry Techniques</u> - The finely-divided co-milled solids components are mixed with water, preferably containing

about 0.1 to 1 wt% surfactant prior to forming and drying the contact soldis product herein. Surface hydrolysis can be a sigificant detriment to many materials, and it is an advantage of the present invention to provide pre-blended, dry-milled materials for dispersion in water and spray dried or otherwise manufactured as dry particles in a short time period, usually less than 1 hour from initial contact with free water.

Hydrolyzable metal oxides and salts are advantageously pre-blended and stored in the substantial absence of added water. It is understood that ostensibly dry components, such as $CaSO_4.H_2O$ (calcium sulfate monohydrate) contain bound water; however, such materials do not interfere with long term storage of pre-blended metal oxide/salt mixtures.

Batchwise or continuous inline feeding of slurry components is well known. Thereafter, the slurry is pumped or otherwise transported to the spray dryer feed tank.

It is a significant advantage of the present invention to use limited amounts of water in forming a fluent slurry for spray drying. By decreasing the amount of water below a weight ratio of 2:1 water:solids (ie - typically 30 wt% or more solids), energy savings are realized in the drying step. By maintaining effectively dry solids in admixture before forming the slurring within, for instance one hour before drying, surface hydrolysis is avoided or minimized.

<u>Surfactants</u> - In the preferred methods, a suitable alkaline stable or acid stable surfactant is added to the slurry. Surfactants for improving the physical and catalystic properties of FCC catalysts are disclosed in US Patent 5,330,943 (Shi et al). Improved attrition resistance and standard testing (ie- Attrition Index or 'AI') are described by Shi et al, who recommend about 0.25-4 grams per 5 kg of spray dried product. Prefered acid stable surfactants are fluorohydrocarbons manufactured

under the trade name "DuPont Zonyl TBS" or 3M "FC-95", and 0.01-1 wt % is satisfactory. The use of surfactant is believed to contribute to attrition resistance by decreasing the 'blow holes' during spray drying.

Spray Drying - Conventional spray drying techniques are known to the industry, usually withdrawing a slurry containing sufficient water to form a fluent mixture of solids and liquid phases, advantageously incorporating a surfactant to impart homogeneity and mechanical properties to the resulting dry products. Heat and low pressure permit flashing or rapid evaporation of the liquid phase from a slurry mist, resulting in agglomeration of smaller particles to form larger solid, typically having a spheroidal shape and a particles size distribution in the 20-250 micron (μ) range or larger. In the manufacture of FCC catalyst or additive solids, the particles typically have an average size of 20-100μ. In sorbent particles for fluid bed processes, a larger particle having an average size of about 150-200μ may be desired.

To exemplify the invention, the following examples are given. In comparative Examples B1-B4 aspects of the invention are demonstrate, contact solids consisting essentially of zinc oxide and calcium sulfate, along with a minor amount of bentonite clay are compounded, dry milled and spray dried to obtain SOx-absorbent particles. In one preferred zinc titanate embodiment, the blended metal oxides contain about 15-65 wt% ZnO, 10-35 wt% TiO_2 and 0-10 wt% bentonite clay or similar binder. In other preferred embodiments, the blended metal compounds contain about 15-65 wt% ZnO, 10-35 wt% $CaSO_4$ and 0-10 wt% bentonite clay. The comminuting step is usually conducted under ambient conditions at a temperature of about -25 to 25°C. The aqueous slurry containing about 35 wt% solids is spray

dried to form agglomerated particles having an average size of about 120-200 microns. The comminuted solids blend is in contact with free water less than 1 hour before the drying step, thereby minimizing hydration reactions.

EXAMPLE A - An attrition-resistant contact solids sulfur oxide sorbent material useful as FCC additive was prepared according to the present invention. A blend of mixed metal oxides, consisting essentially of 21% zinc oxide (ZnO), 14% titanium dioxide (TiO_2), 15% Luzenac 'Cimpact' talc ($Mg_3Si_4O_{10}(OH)_2$), 10% LaRoche hydrotalcite (HTC), and 40% Thiele 'RC-87' kaolin clay, on an oxide basis, was dry blended. The blend of mixed metal oxide powders were fed, using a vibratory tray feeder, to a Sturdevant micronizer jet mill operated under ambient conditons, at air and feed rates to achieve a ground powder average particle size of less than 3 microns, as measured by laser light scattering, ASTM method D4464.

The ground blend of mixed metal oxides was slurried under high shear to achieve 25-30 percent solids dispersin in a solution containing vanadyl sulfate and cerium oxide to equal 2% vanadium and 12% cerium oxide on the finished catalyst. DuPont 'Zonyl TBS' acid-stable fluorohydrocarbon surfactant is added to the spray drier feed at a rate of about 0.1 part per 100 parts of spray dried powder product. The slurry is then spray dried to yield a 70-80 micron (μ) particle product, having an Attrition Index (AI) of 6.

COMPARATIVE EXAMPLES B1-B4 - A series of comparative samples were prepared using the procedure of Example A, except as noted.

EXAMPLE B1 - A blend of mixed metal oxides, consisting of 55 wt% zinc oxide, 9% bentonite, 28% gypsum ($CaSO_4$), and

8% Drierite were dry blended and dry milled in a micronizer to achieve a ground powder average particle size of less than 3 microns. The ground blend of mixed metal oxides was slurried in water to achieve 25-35% solids. Acid-stable surfactant is added, and the slurry is spray dried using a pressure nozzle system to achieve an average spray dried particle of 130µ.

EXAMPLE B2 - Example B1 is repeated, except the preparation is made without surfactant addition.

EXAMPLE B3 - Drierite and calcium sulfate were individually ground to an average particle size of less than 3 microns using the procedure of Example B1. A blend of mixed metal oxides, consisting of 56% unground ZnO, 9% unground Bentonite, 28% ground gypsum, and 7% ground Drierite were dry blended. The blend of powders was slurried in water to 25-35% solids. Acid-stable surfactant is added to the slurry. The slurry is spray dried using a pressure nozzle system to achieve an average spray dried particle of 130µ.

EXAMPLE B4 - Example B3 is repeated, except the preparation is made without the surfactant addition.

TABLE 1

Attrition Data

Materials prepared acccording to Examples B1-B4 are tested for attrition resistance in a standard milling procedure with weight percent loss by attrition being measured at 5 and 20 hour periods.

Example No.	5 hour loss	20 hour loss
B1	5.7 wt%	10.3 wt %
B2	7.4	19.6
B3	8.9	12.4
B4	9.1	13.5

These data show substantial improvement for the co-milled metal oxide materials, especially with addition of the surfactant in Ex. B1. The inventioni s further demonstrated by a series of metal oxide formulations employing the procedure of Example A, except as noted.

EXAMPLE C - A zinc oxide/titanium dioxide mixture having a 1.5:1 $ZnO:TiO_2$ wt.ratio (95 wt%) is blended with 5wt% bentonite and co-milled. The dry milled mixture is slurried with a minor amount of organic binder and surfactant prior to spray drying.

EXAMPLE D - A zinc oxide/titanium dioxide mixture having a 1.5:1 $ZnO:TiO_2$ wt.ratio (35 wt%) is blended with 10% hydrotalcite powder component (LaRoche HTC) having a particle size range of about 4 to 90 microns (predominantly 15-40 microns), produced by the method of US Patent 5,399,329, with 15% talc and 40% fine kaolin clay.

EXAMPLE E - A dry mixture of 40 wt% ultrastable Y zeolite, 20% silica, 10% Grace WCA alumina, and 30 wt% kaolin clay is co-milled and slurried with binder in water. Surfactant is added to feed slurry during spray drying.

EXAMPLE F - A dry mixture of 20 wt% ultrastable Y zeolite, 10% clinotilite clay, 20% silica, 10% Grace WCA alumina, and 40 wt% kaolin clay is co-milled and slurried with binder in water. Surfactant is added to feed slurry during spray drying.

EXAMPLE G - A dry mixture of 10 wt% ZSM-5 zeolite (Alsi-Penta 55), 20% silica, 9% monoammoniuim phosphate, and 61% kaolin clay is co-milled and slurried with Ludox in water. Surfactant is added to feed slurry during spray drying.

TABLE 2

Attrition Data

Materials prepared acccording to Examples C-G are tested for attrition resistance in the standard milling procedure with weight percent loss by attrition being measured by standard A.I. test methods.

Example	Part.Size (microns)	Sur. Area m2/gm.	Attrition Index	D.I./J.I.*
C	96	15	19	22/2.6
D	73	-	4	6/1
E	53	214	24	28/4
F	50	119	11	13/2
G	52	34	1	3/1
B1	120	-	6	7/1

* Davison Index/ Jersey Index

While the invention has been shown by particular examples, there is no intent to limit the inventive concept, except as set forth in the appended claims.

Claims:

1. A method for making solid particles containing a mixture of solid crystalline metal oxide and/or salt compounds comprising the steps of:

admixing particulate metal compounds to form a dry solids blend of at least two different crystalline solids;

comminuting the blended solids by impelling the solids blend with high pressure dry inert gas against a hard plate surface thereby producing finely-divided crystalline solids and recovering a comminuted solids blend having an average particle size of about 1-5 microns;

forming an aqueous slurry of the comminuted solids blend having a weight ratio of free water to solids less than 2:1;

drying the aqueous slurry to form agglomerated particles having an average size range greater than about 20 microns; and

recovering dry agglomerated particles having enhanced attrition resistance and particle size uniformity.

2. The method of Claim 1 wherein the metal compounds comprise about equal parts by weight of calcium sulfate and zinc oxide, and wherein the comminuted solids blend contains at least 50 wt% particles less that 2 microns in size.

3. The method of Claim 2 wherein the blended metal compounds contain about 40-60 wt% ZnO, 40-60 wt% $CaSO4$ and 0-10 wt% bentonite clay; and wherein the aqueous slurry is spray dried to form agglomerated particles having an average size of about 120-200 microns.

4. The method of Claim 1 wherein the comminuted solids blend is in contact with free water less than 1 hour before the drying step, thereby minimizing hydration reactions.

5. The method of Claim 1 wherein the comminuting step is conducted at a temperature of not greater than 25°C.

6. The method of Claim 1 wherein the dry gas has a dew point of less than -50°C.

7. The method of Claim 1 wherein the aqueous slurry contains surfactant comprising acid stable fluorohydrocarbon.

8. A method for making solid particles containing a mixture of solid crystalline calcium sulfate and zinc oxide compounds comprising the steps of:

admixing particulate calcium sulfate and zinc oxide to form a dry solids blend of crystalline solids;

dry milling the blended solids to produce finely-divided crystalline solids;

recovering from the dry milling step a comminuted solids blend having an average particle size of about 1-5 microns;

forming an aqueous slurry containing a surfactant and the comminuted solids blend having a weight ratio of free water to solids less than 2:1;

spray drying the aqueous slurry immediately after adding free water, thereby forming agglomerated particles having an average size range greater than about 20 microns; and

recovering dry agglomerated particles having enhanced attrition resistance and particle size uniformity.

9. The method of Claim 8 wherein the crystalline solids comprise about equal parts by weight of calcium sulfate and zinc oxide, and wherein the comminuted solids blend contains at least 50 wt% particles less that 2 microns in size.

10. The method of Claim 9 wherein the blended metal compounds contain about 40-60 wt% ZnO, 40-60 wt% anhydrous and/or hydrated CaSO4, and 0-10 wt% bentonite clay; and wherein the aqueous slurry is spray dried to form agglomerated particles having an average size of about 20-200 microns.

11. The method of Claim 8 wherein the comminuted solids blend is in contact with free water less than 1 hour before the drying step, thereby minimizing hydration reactions.

12. The method of Claim 8 wherein the aqueous slurry contains 0.01-1 wt% surfactant comprising acid stable fluorohydrocarbon.

13. A method for making fluidizible solid catalyst particles containing a mixture of catalytically-active solid crystalline metal oxide material and at least one other crystalline material comprising a metal compound comprising the steps of:

admixing coarse particulate metal materials to form a dry solids blend of at least two different particulate crystalline solids;

comminuting the blended solids by impelling the solids blend with high pressure dry inert gas against a hard plate surface thereby producing finely-divided crystalline solids

and recovering a comminuted solids blend having an average particle size less than 2 microns;

forming an aqueous slurry of the comminuted solids blend containing an acid stable fluorohydrocarbon surfactant;

drying the aqueous slurry to form agglomerated particles having an average size range greater than about 20 microns; and

recovering dry agglomerated catalytic particles having enhanced attrition resistance and particle size uniformity.

14. The method of Claim 13 wherein the metal oxide material comprises a cracking catalyst additive.

15. The method of Claim 13 wherein the metal oxide material comprises zeolite cracking catalyst.

16. A method for making solid particles containing a mixture of solid crystalline metal oxide and/or salt compounds comprising the steps of:

admixing particulate metal compounds to form a dry solids blend of at least two different crystalline solids;

dry milling the blended solids to produce finely-divided crystalline solids;

recovering from the dry milling step a comminuted solids blend having an average particle size of about 1-5 microns;

storing the recovered comminuted solids blend in a dry storage container for subsequent completion of manufacture;

transporting a measured portion of the comminuted solids blend from the storage container to a manufacturing facility;

forming an aqueous slurry of the transported, comminuted solids blend;

drying the aqueous slurry to form agglomerated particles having an average size range greater than about 20 microns; and

recovering dry agglomerated particles having enhanced attrition resistance and particle size uniformity.

17. The method of Claim 16 wherein the dry milling step is conducted in a micronizer comminuting mill.

18. The method of Claim 16 wherein a plurality of different comminuted solids blends are transported from storage containers and admixed in the aqueous slurry.

19. The method of Claim 16 wherein the comminuted solids blend is in contact with free water less than 1 hour before the drying step, thereby minimizing hydration reactions.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US98/18169

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :C01B 7/00; B01J 8/00
US CL :423/244.01, 244.06, 244.08; 502/64, 68, 80, 514
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 423/244.01, 244.06, 244.08; 502/64, 68, 80, 514

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5,498,731 A (TSURITA et al.) 12 March 1996 (12-03-96), column 4, line 43 - column 7, line 67.	1 & 4-6
Y	US 5,559,067 A (LERNER et al.) 24 September 1996 (24-09-96), column 5, line 40 - column 9, line 41.	1, 4-7, 13-19
Y	US 5,330,943 A (SHI et al.) 19 July 1994 (16-07-94), see the entire document.	1-19
Y	US 5,512,097 A (EMMER) 30 April 1996 (30-04-96), column. 4-6.	1-12
Y	US 4,931,264 A (ROCHELLE et al.) 05 June 1990 (05-06-90), column. 14, lines 5-50.	1-12
Y	US 4,640,825 A (ROSENBERG) 03 February 1987 (03-02-87), column. 5-7.	1-12

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

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Date of the actual completion of the international search	Date of mailing of the international search report
21 DECEMBER 1998	12 JAN 1999

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